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X-616-69-497

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NASA TM X- 63751

**LYMAN- α FLUORESCENCE
FROM THE
PHOTODISSOCIATION OF H₂**

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NOVEMBER 1969



**GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND**

N70-12927

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
	26	1
	(PAGES)	(CODE)
	TMX 63751	24
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

LYMAN- α FLUORESCENCE FROM THE PHOTODISSOCIATION
OF H_2

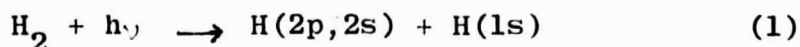
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Photodissociation and fluorescence cross sections for H_2 have been measured from 860 to 700 \AA by observing the Lyman- α photons emitted at 90° to an incident photon beam. The photodissociation quantum efficiency was found to be unity from 850 \AA to the photoionization threshold at 804 \AA and about 10% at shorter wavelength. By observing the fluorescence radiation as a function of decreasing pressure, it was determined that most of the excited H atoms were formed in the metastable 2s state and that the Lyman- α emission results primarily from collisional quenching. The ratio of the collisional cross section with and without Lyman- α emission was measured for different relative velocities and was found to increase appreciably with increasing velocity.

I. INTRODUCTION

Since the work of Hopfield¹ in 1930 the absorption of photons by molecular hydrogen below 1000 Å has been a subject of considerable interest. This interest stems from the fact that H₂ as the simplest molecule is the most amenable to theoretical calculations and to interpreting experimental data. Aside from its fundamental interest in physics, the absorption properties of hydrogen are of importance to planetary atmospheres. For example, the Mariner 5 observations of the Lyman- γ (L $_{\gamma}$) emission from Venus have generally been interpreted as arising from two components of its exosphere whose scale heights differ by a factor of two. Barth, et. al.² initially suggested that the two components were H and H₂. The emission then results from the resonant scattering of solar L $_{\gamma}$ by atomic hydrogen and from photodissociative excitation of H₂ by solar radiation of wavelength shorter than 849 Å. Barth³ has since suggested that possible alternatives could be atomic hydrogen and deuterium or two atomic hydrogen components at different temperatures. Each of these alternatives have difficulties associated with them.⁴⁻⁶ What is needed to assess the merits of the

first proposal, i.e., H and H₂, are cross sections for the process



as a function of wavelength.

The absorption spectrum of H₂ below 1000 Å is characterized by a sudden large increase in its absorption coefficient in the vicinity of 850 Å which corresponds to the onset of the photodissociation continuum. For a transition from the lowest rotational energy level (J''=0-J'=0) the threshold occurs at 844.8 Å. However, because of the population of higher lying ground state rotational energy levels at room temperature, the effective threshold is shifted to 857.3 Å⁷ (J''=5-J'=0). It has been shown by Namioka⁸ that the photodissociation edge corresponds to a transition into the continuum of the B'¹Σ⁺ electronic state. At shorter wavelengths the C'¹Π_u and B'¹Σ_u⁺ states also contribute to the continuum so that both H(2p) and metastable H(2s) atoms are produced.

Superimposed on the photodissociation continuum is a strong absorption due to the X'¹Σ_g⁺ - D'¹Π_u transition plus a weaker absorption due to the D' electronic state. Although it has long been known that the D'¹Π_u state predissociates for v' ≥ 3, the Q-branch lines remain

sharp as do the absorption lines for the X-D' transition.⁹ Therefore, it can not be assumed that the quantum efficiency for photodissociation is unity below 857 Å.

Although the absorption and photoionization spectrum of H₂ has been extensively studied, few direct measurements have been made of the L_α fluorescence. The first measurements were those of Cook and Metzger¹⁰ who observed the total fluorescence radiation by placing a sodium salicylate coated photomultiplier at right angles to the incident photon beam. With a resolution of 2.5 Å they observed a fluorescence threshold at about 857 Å but were unable to observe the change in fluorescence with wavelength because of an unfavorable signal to noise ratio. Beyer and Welge¹¹ were able to improve on the measurements of Cook and Metzger by using a solar blind photomultiplier as the fluorescence detector and substituting various window materials to determine the wavelength range of the fluorescence radiation. Because they used a line source for their background radiation, Beyer and Welge were only able to observe the general trends in the fluorescence cross section. Recently Comes and Wellern¹² have reported fluorescence measurements using a continuum light source. By

assuming that only L_{α} was emitted they were able to arrange the geometry of their experiment so that a large fraction of the fluorescence radiation was collected by their detector. Relative fluorescence cross sections were obtained with a resolution of 0.5 \AA which were then normalized by assuming that the fluorescence quantum efficiency is unity at the D-X absorption peaks.

The measurements reported here were obtained with a continuum background light source and an apparatus basically similar to that of Comes and Wellern. However, rather than assuming that only L_{α} was emitted, an oxygen filter was placed between the fluorescence detector and the absorption cell so that its sensitivity was restricted to 1215.7 \AA . Also, an electric field was applied to the fluorescence region so that the metastable 2s atoms were detected as well as those formed in the 2p state. The fraction of atoms produced in the 2p state was then determined in a separate experiment. Finally, a direct calibration of the experiment was obtained by comparing the signal obtained from the Rayleigh scattering of L_{α} by Xe with the fluorescence signal.

II. EXPERIMENTAL

A schematic diagram of the apparatus is shown in Figure 1. Briefly, the Hopfield helium continuum was produced in a π shaped water cooled discharge tube at a pressure of 30 Torr. The continuum was excited by discharging a 2000 pf capacitor charged to 10 kv through the lamp at a repetition rate of 5000 Hertz using an external spark gap trigger. The firing of the spark gap also produced a timing pulse which was fed into a Hamner Model NS-1 scaler so that the total number of discharges for a fixed time interval could be measured. The helium pressure, discharge voltage, and repetition rate was monitored throughout the experiments and was maintained constant to within $\pm 5\%$. A spectrum of the helium continuum is shown in Figure 2. In the spectral region of interest the only impurity line was a weak feature, possible due to CII, at 858 \AA . The absolute photon flux through the absorption cell was determined by measuring the photo-ionization current when Xe was placed in the absorption cell. With a 1 \AA bandpass the peak photon flux was found to be 8×10^6 photons/sec.

The background radiation was dispersed by a 1 meter normal incidence McPherson Model 220 monochrometer

equipped with a 600 line/mm platinum coated grating blazed at 800 Å. Using 40 μ wide entrance and exit slits, the monochromator had a measured resolution of 1 Å. The monochromator was isolated from the light source by a differential pumping chamber so that with a pressure of 30 Torr in the lamp the pressure in the monochromator was 2×10^{-4} Torr.

Attached to the exit slit of the monochromator was a 52.5 cm long stainless steel absorption cell. Light passing through this cell was monitored using a sodium salicylate coated photomultiplier tube. The gas pressure was measured with an MKS Baratron capacitance manometer which had been calibrated against a trapped McCloud gauge.

A viewing port with a LiF window 15.5 cm from the exit slit allowed the L_{α} fluorescence radiation emitted at right angles to the incident photon beam to be observed by means of an iodine-vapor-filled ultraviolet photon counter¹³ preceded by a flowing oxygen filter. In the wavelength range over which the detector is sensitive (1100 - 1260 Å), oxygen is a strong absorber except for a narrow window centered at 1215.7 Å.¹⁴ A further consequence of the oxygen filter was that it restricted the field of view of the detector to essentially that radiation emitted normal to the incident photon beam. The output pulses from the photon detector

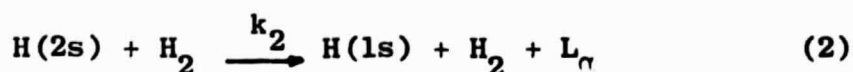
were amplified by a Hewlett Packard Model 5554A charge sensitive preamplifier and fed into a Hamner Model NS-1 scaler. Both of the scalers used in these experiments were synchronously controlled by the same Hamner Model NS-1 timer.

The lifetime of the $H(2s)$ atoms is strongly influenced by the presence of an electric field. To guard against the presence of stray fields a cylindrical copper mesh was placed inside the absorption cell and held at ground potential. As an additional precaution against fields arising from the photon detector a second electrostatic shield (not shown in Figure (1)) was placed between the iodine detector and the O_2 filter. When it was desired to detect the metastable atoms an electric field was applied by means of two parallel plates inside the cell.

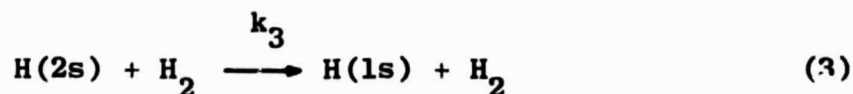
The gases used in these experiments were Air Products High Purity hydrogen and Air Products Research Grade xenon. The xenon was used without further purification while the hydrogen was first passed through a liquid nitrogen cooled trap.

III. RESULTS AND DISCUSSIONS

The photodissociation of H_2 results in the production of a ground state $H(1s)$ atom plus either an $H(2p)$ or $H(2s)$ atom. The $H(2p)$ atoms decay to the ground state emitting a L_{α} photon with a lifetime $\tau_{2p} = 1.6 \times 10^{-9}$ sec while the $H(2s)$ atoms are metastable with a lifetime of 1.4×10^{-15} sec¹⁵. The metastables are deactivated by collisions with H_2 . In one case a L_{α} photon is emitted



while in the other the excess energy is removed through other processes



Let $I_0(\lambda)$ signify the incident light intensity at a wavelength λ , σ_{pd} and σ_{ab} the photodissociation and absorption cross sections, k_2 and k_3 the rate constants for reactions (2) and (3) respectively, L the absorption path length, $[H_2]$ the number density of H_2 , and F the fraction of the excited atoms formed in the $2p$ state. Then, solving the steady state rate equations, the fluorescent light intensity is

$$I_{L_{\alpha}}(\lambda) = \frac{\sigma_{pd}}{\sigma_{ab}} I_0(\lambda) (1 - \exp(-\sigma_{ab} \cdot [H_2] \cdot L)) (F + \frac{(1-F)k_2}{k_2 + k_3}) \quad (4)$$

For pressures less than 0.02 Torr the exponential can be replaced by the first two terms in its series expansion so that

$$I_{L_{\gamma}}(\lambda) = \sigma_{pd}(\lambda) I_0(\lambda) [H_2] L \left(\frac{k_2 + k_3 F}{k_2 + k_3} \right) \quad (5)$$

The fluorescence thus depends not only on the fraction of atoms formed in the 2p state but also on the fraction of the metastable 2s atoms which emit L_{γ} as a result of collisional quenching.

The lifetime of the H(2s) atoms is altered drastically by the presence of an electric field. For a field of E V/cm the resulting lifetime becomes¹⁶

$$\tau_{2s}' = 1/2780 E^2 \text{ sec} \quad (6)$$

For an electric field > 60 V/cm the lifetime is much shorter than the time between collisions. Then,

$$I_{fl}(\lambda) = \frac{\sigma_{pd}}{\sigma_{ab}} I_0(\lambda) (1 - \exp(-\sigma_{ab} L [H_2])) \approx \sigma_{pd} I_0(\lambda) H_2 L \quad (7)$$

and the photodissociation cross section can be determined directly by observing the fluorescence light intensity.

The results of the measurement of photodissociation cross sections are presented in Figure 3. For comparison, total absorption cross sections obtained with the same resolution (1.0 Å) are also given. The photodissociation cross sections were obtained with a

quenching field of 100 V/cm and a pressure of 15.0 + 0.5 μ . Data were taken at 0.5 \AA intervals with an integrating time of 200 sec at each point. To put the relative cross sections on a absolute basis, the L_{γ} fluorescence signal at 839.2 \AA was compared with the signal obtained from the Rayleigh scattering of L_{γ} radiation by Xe. Since the detector and collection geometries were the same in each case,

$$\sigma_{\text{pd}}(839.2\text{\AA}) = 1.10 J_{\text{RS}} \frac{I_{\text{O}}(1215.7\text{\AA})}{I_{\text{O}}(839.2\text{\AA})} \frac{P(\text{Xe})}{P(\text{H}_2)} \frac{I_{\text{f1}}}{I_{\text{RS}}} \quad (8)$$

The factor of 1.10 in Equation (8) results from the polarization of the L_{γ} emission in the presence of an electric field. Then the light intensity observed at 90° to the electric field is related to the total intensity by¹⁷

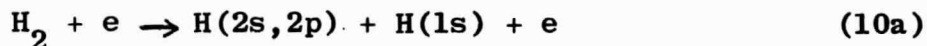
$$I_{\text{T}} = 4\pi I(90^{\circ}) (1 - P/3) \quad (9)$$

P , the polarization, has been measured by Fite et.al.¹⁸ who quotes a value of -0.30 ± 0.02 so that

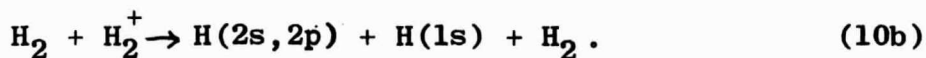
$I_{\text{T}} = 1.10(4\pi)I(90^{\circ})$. A fresh sodium salacylate coating was used in the calibration to insure that the sensitivity of the photomultiplier used to measure I_{O} was independent of wavelength¹⁹. Using Marmo, et. al.²⁰ value of $1.26 \times 10^{-22} \text{ cm}^2$ for σ_{RS} , the photodissociation quantum yield was found to be 1.2 ± 0.2 . Within the experimental error, all the photons absorbed at 839.2 \AA result in an excited H atom.

The relative accuracy of the photodissociation cross section is $\pm 10\%$ at the absorption peaks and $\pm 20\%$ at the minimums while the accuracy of the absorption cross sections is $\pm 10\%$. The absorption coefficients are in excellent agreement with those of Cook and Metzger¹⁰ and with those of Huffman²¹ which were obtained under higher resolution (0.25 \AA). There is also excellent agreement with Delgarno and Allis's²² calculated photodissociation cross sections for the underlying continuum. Within the limit of the experimental error the photodissociation quantum efficiency is unity between 860 and about 804 \AA which is consistent with the well known fact that the $D^1\Pi_u$ state of H_2 is strongly predissociated.

At 804.1 \AA the H_2 absorption coefficient increases because of preionization of the $D^1\Pi_u$ state. Because photoelectrons and ions were formed in the presence of the quenching field, a fraction of the L_α signal must arise as a result of the excitation processes



and



The ratio of the L_α intensity due to excitation by electron and ion impact, (I_{ex}), to the intensity from photodissociation is

$$\frac{I_{ex}}{I_{fl}} = \frac{\sigma_{ion}(\lambda)}{\sigma_{pd}(\lambda)} \sigma_{ex}(\lambda) [H_2] \times \quad (11)$$

Here $\sigma_{ex}(\lambda)$ is the total cross section for reactions (10) and X is the path length of the electrons or ions through the gas. If it is assumed that $\sigma_{pd} = \sigma_{ab} - \sigma_{ion}$ and that the cross section for (10b) is equal to that for (10a), then the data of Cook and Metzger¹⁰ and Fite and Brackmann²³ can be used to calculate I_{ex}/I_{fl} . The results of this calculation are shown in Figure 4 from which it is seen that the error resulting from photoionization becomes comparable to the statistical error only at wavelengths shorter than 720 Å. The photodissociation cross sections in Figure 3 have been corrected for the L_{α} emission due to electron and ion impact with H_2 .

The fraction of the excited H atoms formed in the 2p state can be determined by measuring the ratio $I_{fl}(\lambda)/I_{fl}(\lambda)$ as a function of decreasing pressure. At sufficiently low pressure ($\sim 1 \mu$) the H(2s) atoms diffuse out of the field of view of the detector except for a small fraction which may emit L_{α} radiation through collisional deactivation with the walls. From Figure 5 it is seen that at most 15% of the excited atoms are formed in the 2p state. A theoretical estimate can be made of F if it is assumed that the H(2p) atoms come from the photodissociation continuum of the $C^1\Pi_u$ and $B^1\Sigma_u^+$ states while the H(2s) atoms arise from the $B'^1\Sigma_u^+$. Then, using Delgarno and Allison calculations and assuming the $B'^1\Sigma_u^+$ state is the perturber of the $D^1\Pi_u$, F approximately equals .05 at the absorption peaks. Considering the modest statistical accuracy due

to the low counting rates at pressures below 5μ (<5 counts/min), there is reasonable agreement with the theoretical prediction. In any event, at the absorption peaks most of the excited atoms result from the predissociation of the $D^1\Pi_u$ state and the experimental results demonstrate that these are the metastable $H(2s)$ atoms. This is not true at the absorption minimums where the relative contributions of the B and C states are much larger. Delgarno and Allison calculations indicate that at the absorption minimums 30% of the excited dissociation products are formed in the $2p$ state. Unfortunately the fluorescence signals were too small to measure this ratio experimentally.

From Equation (5) an effective fluorescence cross section

$$\sigma_{fl} = \frac{\frac{k_2}{2} + \frac{k_3 F}{3}}{\frac{k_2}{2} + \frac{k_3}{3}} \sigma_{pd} = \frac{\sigma_2 + \sigma_3 F}{\sigma_2 + \sigma_3} \sigma_{pd} \quad (12)$$

can be defined and the coefficient $(\sigma_2 + \sigma_3 F)/(\sigma_2 + \sigma_3)$ determined by observing the fluorescence with and without a quenching field. Since most of the H atoms are formed in the $2s$ state, i.e. $F \approx 0$, the fluorescence cross section is determined by the fraction of atoms which emit L_α when collisionally quenched. The ratio of fluorescence to photodissociation cross sections

is presented in Figure 6 where it is clearly seen that most of the quenched atoms emit L_{α} radiation. This fact is not surprising as σ_2 has been measured at room temperature by Fite et. al.²⁴ who found that $\sigma_2 = 0.7 \times 10^{-14} \text{ cm}^2$. The magnitude of σ_2 implies that a L_{α} photon is emitted in nearly every collision between a H(2s) atom and a H_2 molecule.

The fluorescence cross sections obtained in this work compare favorably with the previously reported values of Beyer and Welge¹¹ and Comes and Wellern.¹² This agreement may be somewhat fortuitous, however, as in the previous works an electric field from their photon detector may have penetrated to the fluorescence region. If this was the case, their measurements may represent photodissociation cross sections rather than fluorescence cross sections.

Finally, the data in Figure 6 can be re-plotted to give σ_2/σ_3 as a function of the relative velocity of the H atoms with respect to the H_2 molecules. These results are compared in Figure 7 with those of Comes and Wenning²⁵ who made measurements somewhat similar to those described here but who used a different data reduction technique. Briefly, Comes and Wenning observed the variation of I_{f1} as a function of quenching field - keeping the pressure fixed. Then using a digital computer, all parameters were adjusted in a completely general expression for I_{f1} until a best

fit was obtained to the experimental data. Their results are presented in Figure 7 and lie appreciably lower than the present work. However, Comes and Wenning do not estimate the accuracy of their measurements so it is not known if this discrepancy is significant.

Returning now to Barth's interpretation of the Lyman- α observations of Venus, there are two questions relevant to the present investigation: The first question is Barth's use of Cook and Metzger's total absorption cross sections to infer photodissociation cross sections and the second is Barth's assumption that the photodissociation results in excited H(2p) atoms. Equating the absorption and photodissociation cross sections has been shown to be experimentally valid, even where the H_2 $X^1\Sigma - D^1\Pi_u$ transition is superimposed on the photodissociation continuum. However, most of excited H atoms are formed in the metastable 2s state so the pertinent question then becomes what fraction of the collisionally quenched H(2s) atoms emit L_α radiation. For collisions with H_2 molecules this number has been shown to be on the order of 75% although for collisions with CO_2 this fraction could be somewhat different. Thus the arguments either for or against Barth's hypothesis remain essentially unchanged by these experiments.

FOOTNOTES

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FIGURE CAPTIONS

- Figure 1 Schematic diagram of the apparatus used to observe the Lyman- α fluorescence resulting from the photodissociation of H_2 .
- Figure 2 Spectrum of the He condensed spark discharge.
- Figure 3 Photodissociation and total absorption cross sections for H_2 . The long dashed curve is Delgarno and Allison's calculated values for the underlying photodissociation continuum.
- Figure 4 Plot of the variation with wavelength of the Lyman- α intensity arising from photoelectron and ion dissociative excitation of H_2 divided by the Lyman- α fluorescence intensity.
- Figure 5 Ratio of the Lyman- α fluorescence intensity in a field free region, to the fluorescence in an electric field of 100V/cm. Extrapolation to zero pressure gives an upper limit to the fraction of excited H atoms formed in the 2p state.
- Figure 6 Ratio of the fluorescence cross section to the photodissociation cross section as a function of wavelength.
- Figure 7 Variation of the ratio of the collisional quenching cross section with and without Lyman- α emission as a function of velocity.

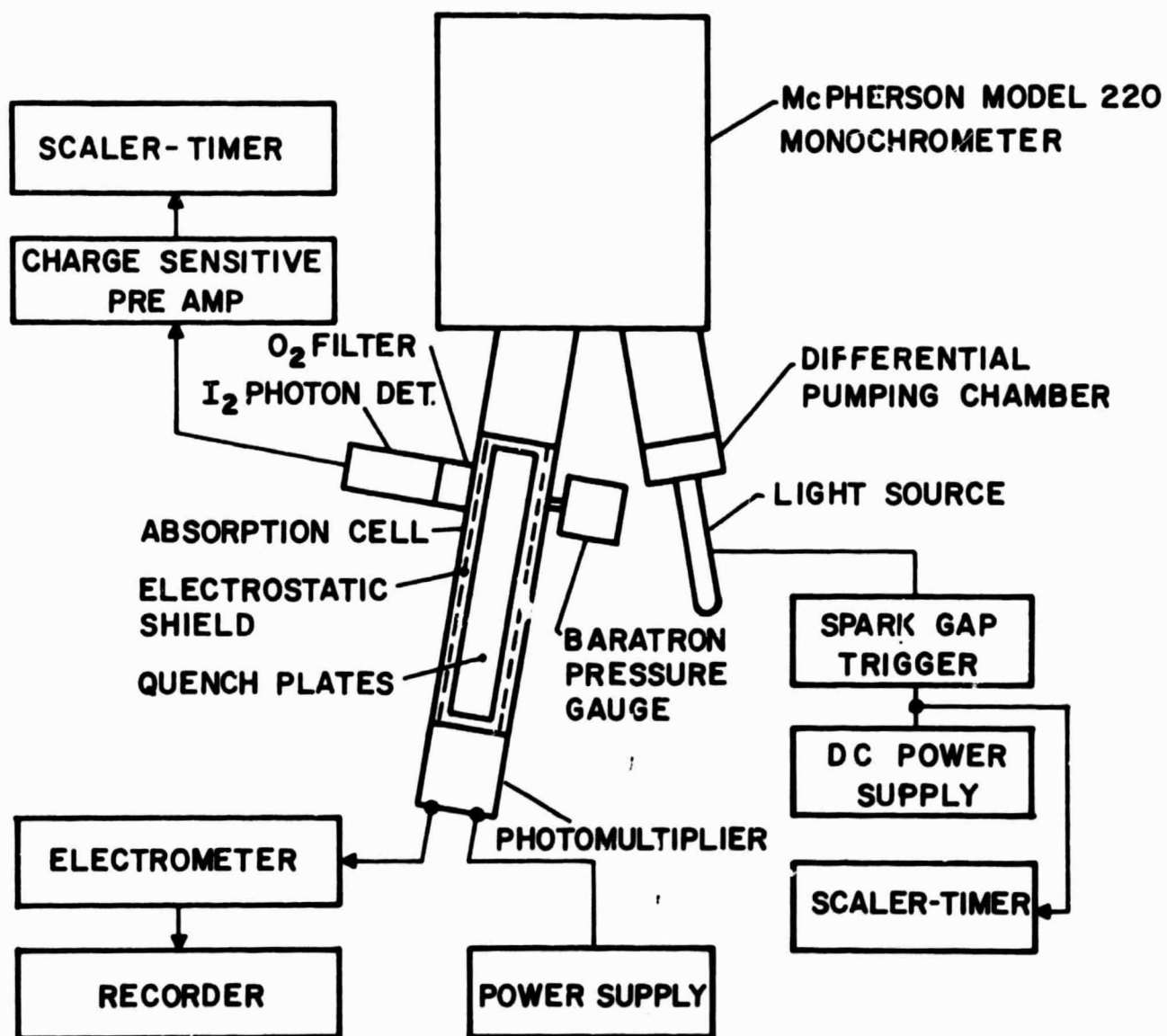


Figure 1

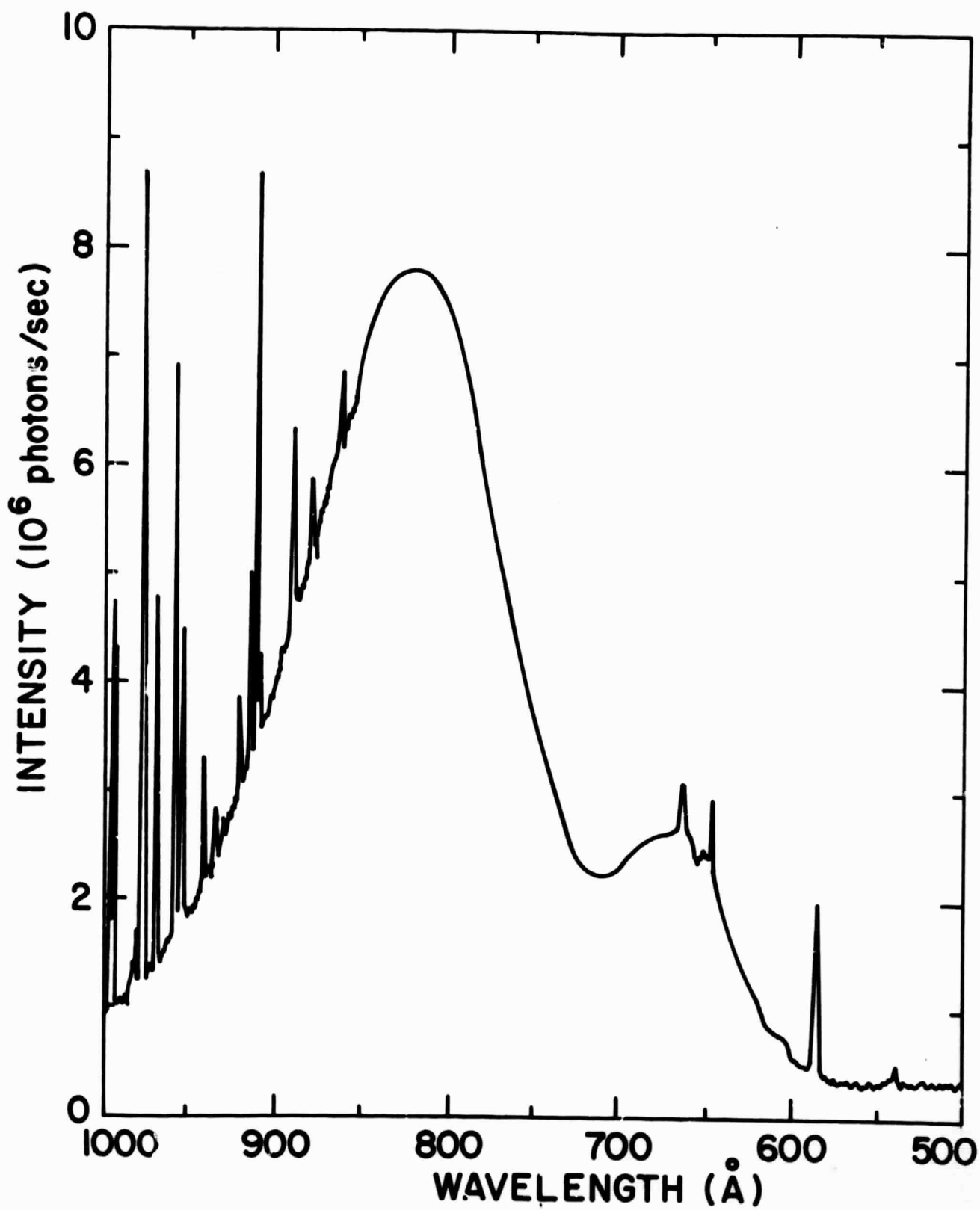


Figure 2

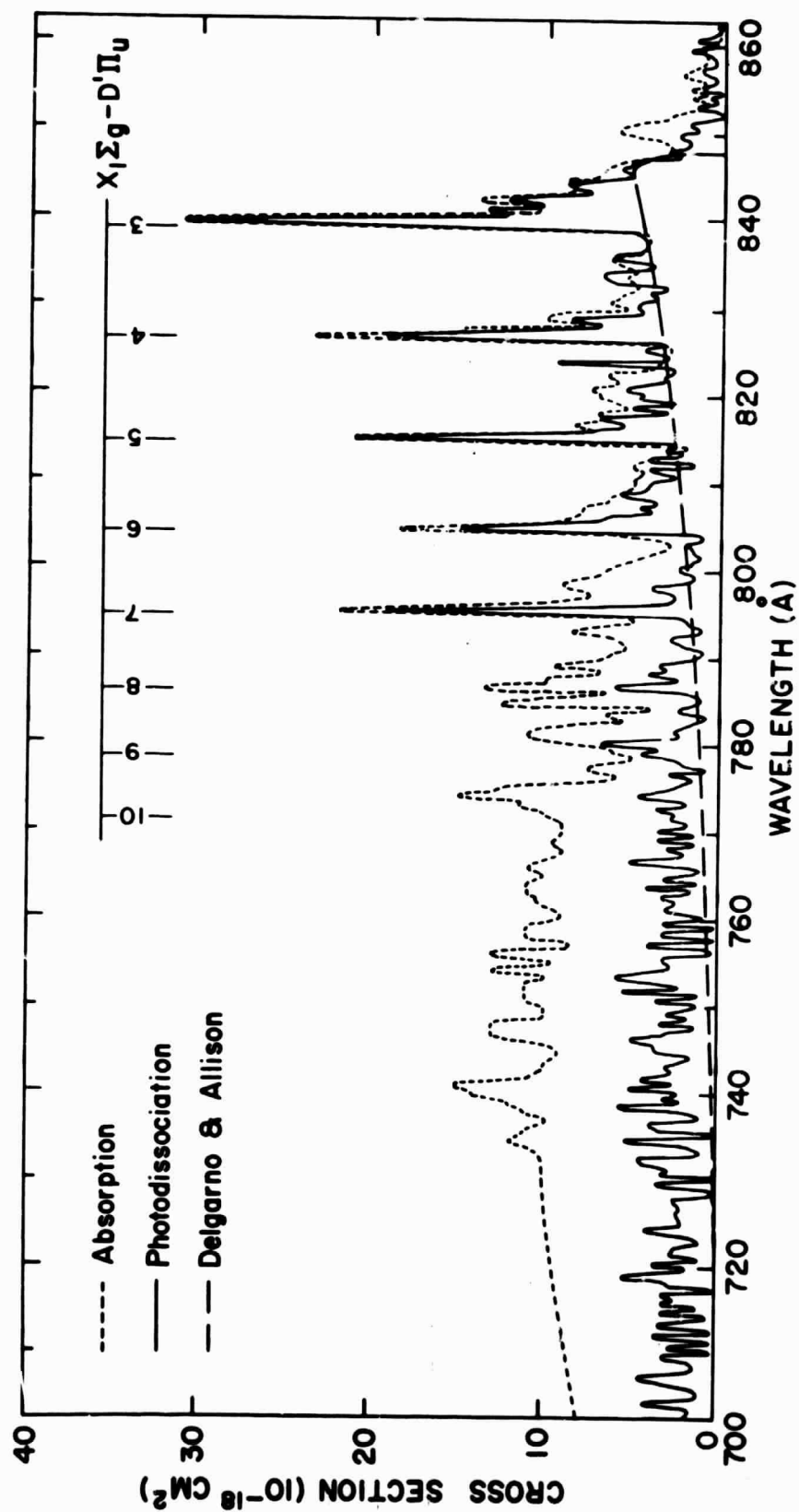


Figure 3

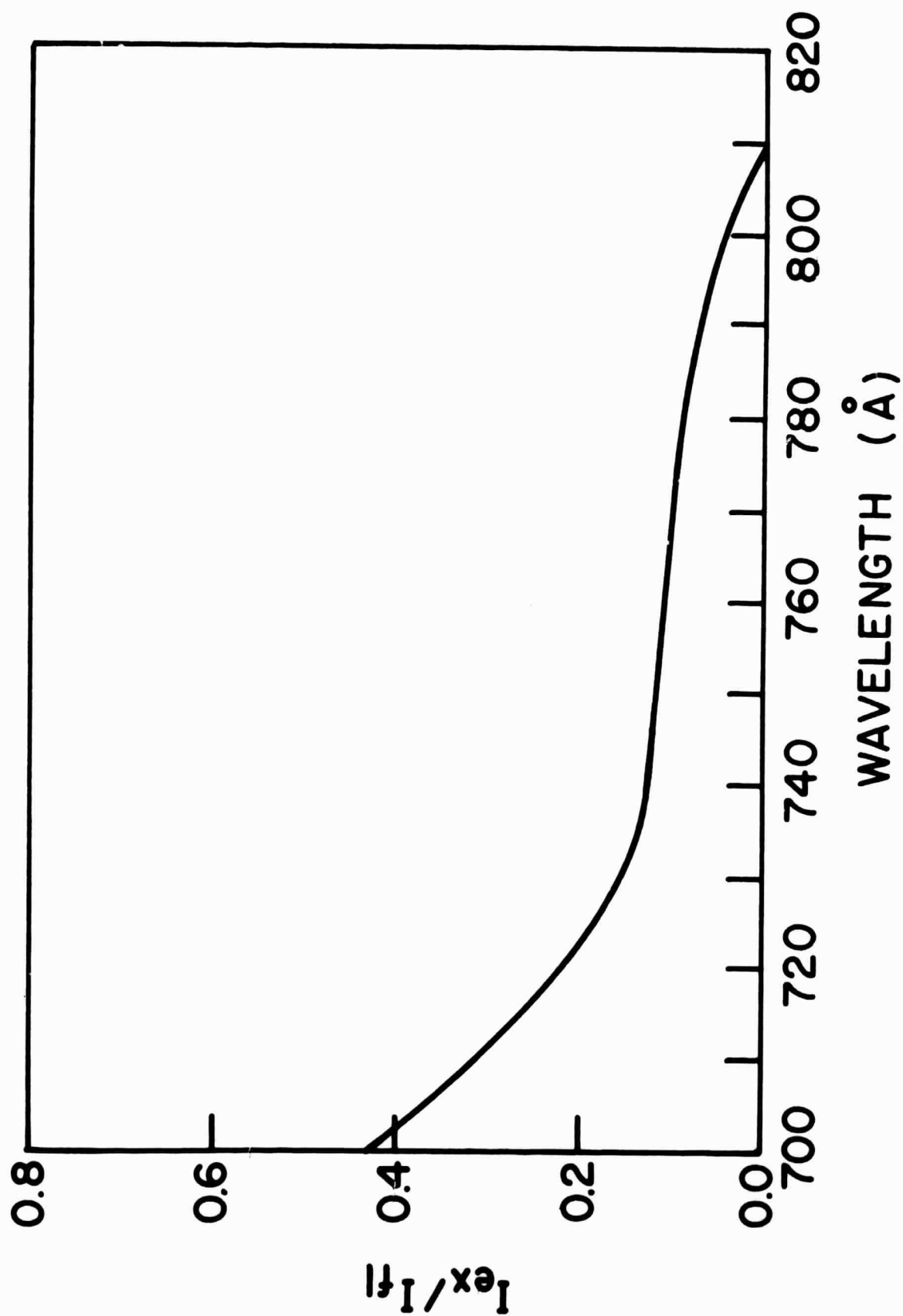


Figure 4

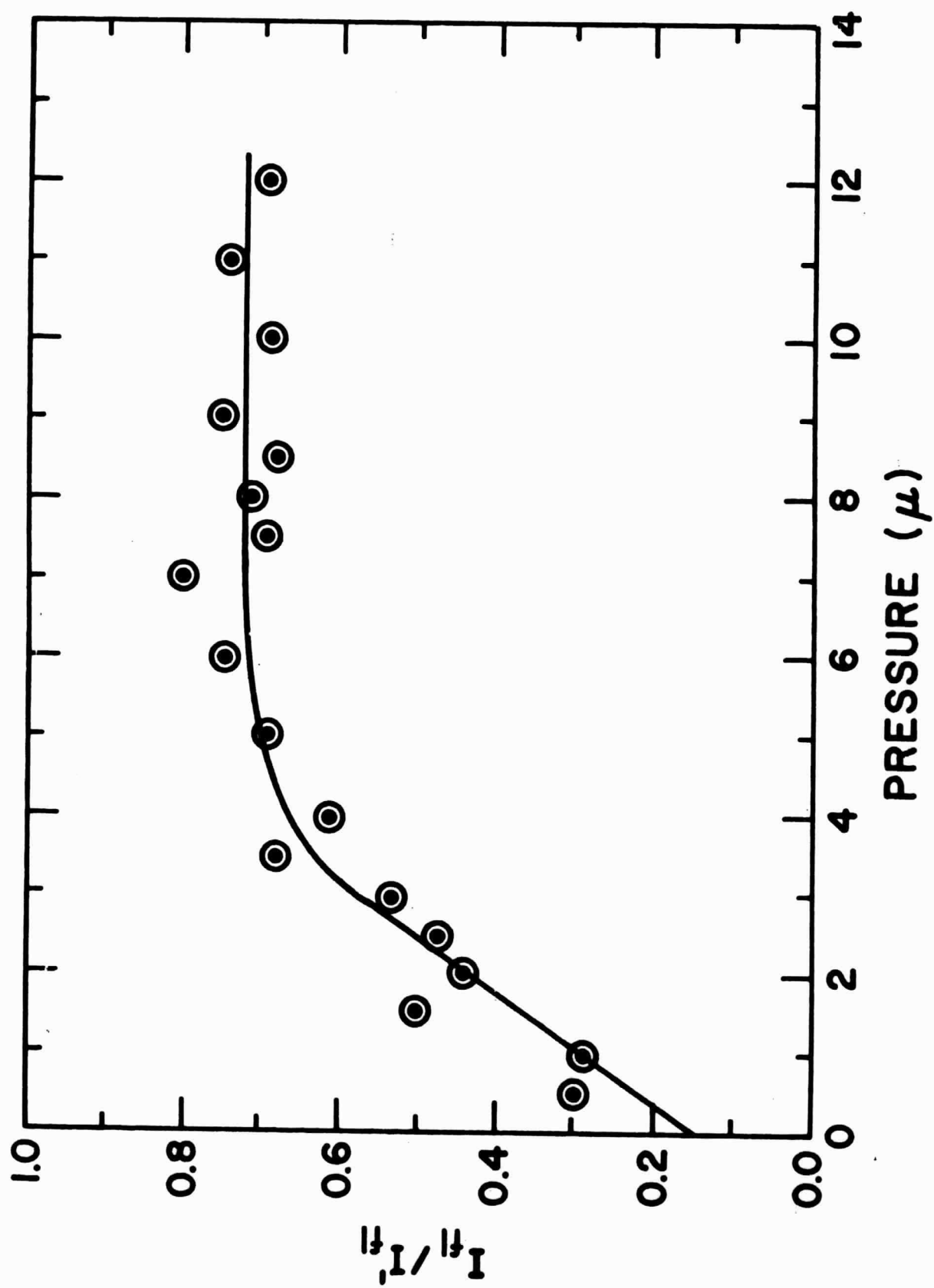


Figure 5

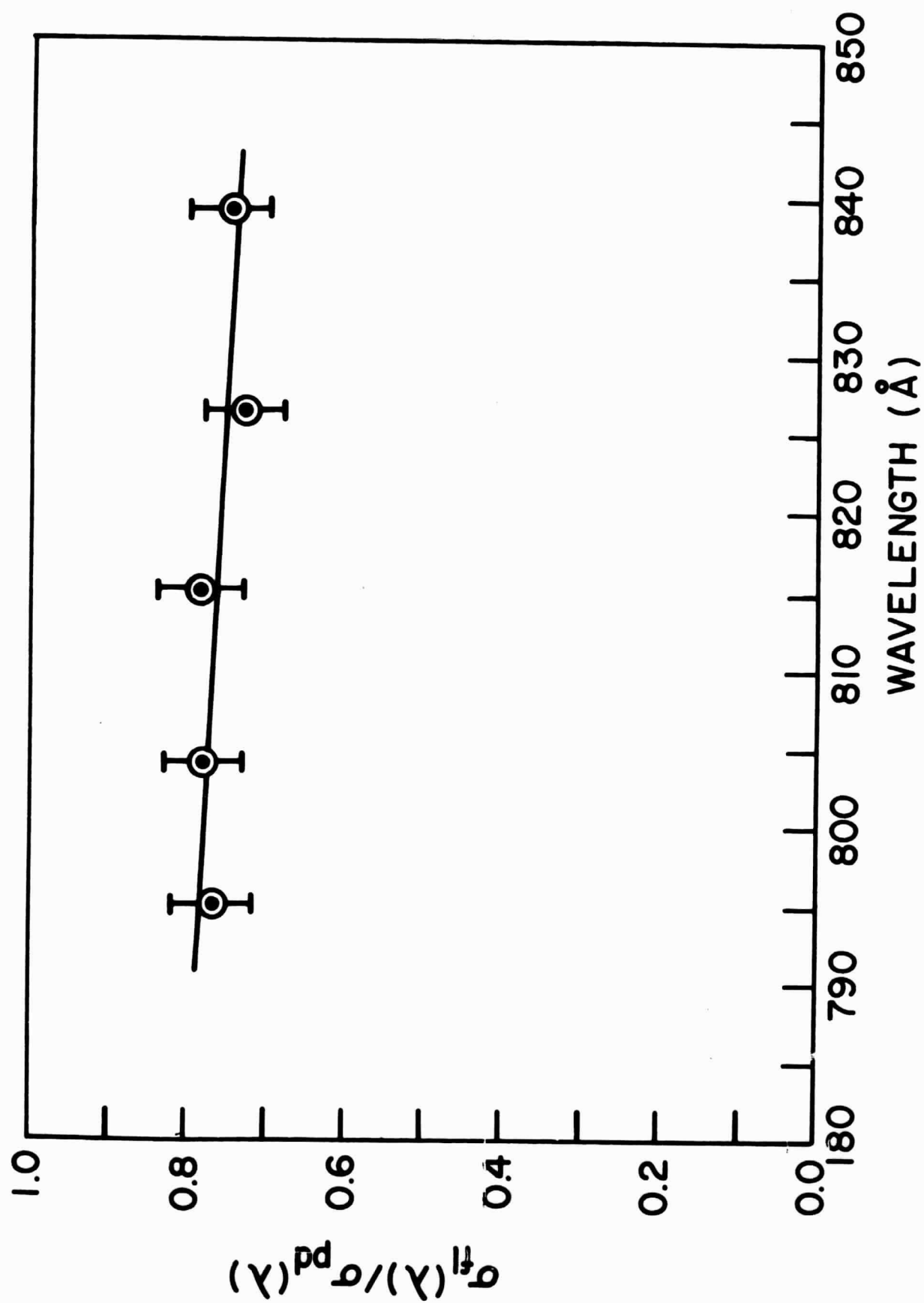


Figure 6

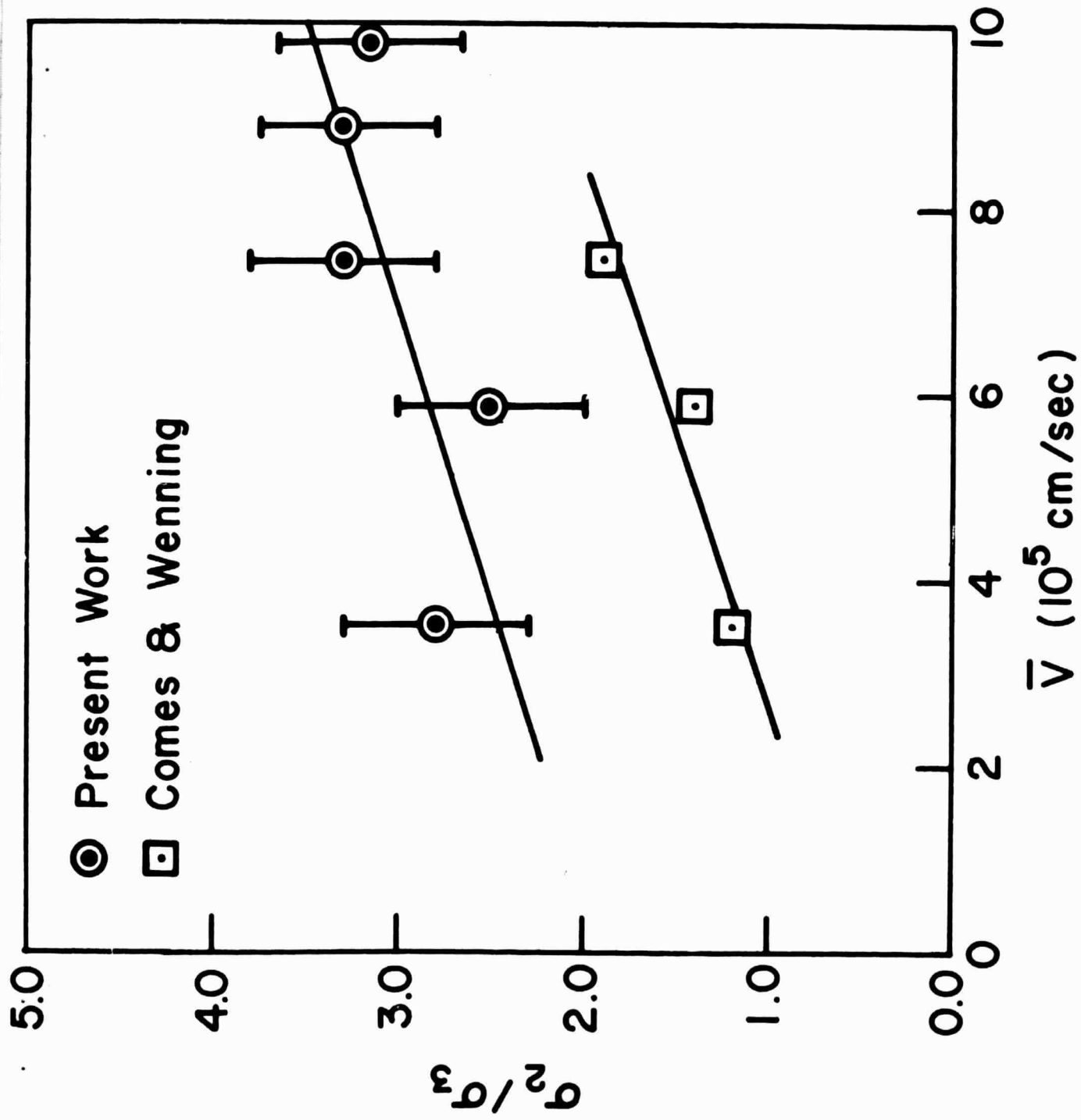


Figure 7